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Effect of Electrodeposition Condition on GMR Co/Cu Multilayers

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Co/Cu GMR multilayers were electrodeposited from various electrolytes using the dual bath technique to achieve high sensitive GMR multilayers. GMR ratio and sensitivity were strongly influenced by solution compositions and electrodeposition parameters where GMR and sensitivity of 12% and 0.052%/Oe were achieved from pyrophosphate baths. The effect of plating conditions on properties of Co/Cu multilayers may be attributed to crystallinity and grain size of deposits, and the ability of plating solutions to deposit contiguous films at lower nano thicknesses.

Keywords : giant magnetoresistance, electrodeposition, multilayer

1. Introduction

Nanostructured materials provide unique properties for applications in electronics, spintronics and photonics. Giant magnetoresistive (GMR) materials are an example where the change of electrical resistance ($\Delta\rho/\rho$) can be "tailored" by controlling individual layer thicknesses. Many practical applications of GMR materials have included reading heads in computer disk drives, magnetoresistive random access memory (MRAM), tape heads in consumer products such as digital compact cassettes (DCC), magnetometers, compass systems, current measurement in cable and position detection and/or the speed of moving parts, which are equipped with hard magnets [1]. Sensors based on GMR materials can be miniaturized providing low impedances suitable for electronic processing with low electromagnetic noise and interference. GMR materials also have a greater MR ratio (max. 70%) than anisotropic magnetoresitive (AMR) thin films (max. 2%) with faster access time [1].

GMR effects result from an exchange interaction between nano-thick magnetic layers separated by nonmagnetic layers where adjacent magnetic layers can be either ferromagnetically or antiferromagnetically coupled [1]. The strength of interlayer coupling depends on layer thickness and oscillates with the nonmagnetic layer thickness [2].

The relationship between the GMR effect and interlayer coupling indicates that high GMR effects can only be expected in strongly coupled antiferromagnetic thickness regimes, resulting in intrinsically small sensitivity: i.e. the change in GMR as a function of the change in applied magnetic field ($d(\Delta\rho/\rho)/dH$) [1].

Electrodeposition is a cost effective process to fabricate various magnetic films including soft, hard and nanostructured magnetic films. Electrodeposition has many advantages over vacuum processes: low cost, easy scale up and maintenance, and low (near room) temperature operating conditions. Vacuum processes may be as much as ten times more costly than electrodeposition [3]. Schindler *et al.* reported that high quality thin film magnetic electrodeposits can be produced which are equivalent to vacuum films deposited at 5×10^{-10} mbar pressure [4]. We have demonstrated that various IC compatible high performance hard magnetic films can be electrodeposited [5].

Ross [6], and Schwarzacher and Lashmore [7] have reviewed on electrodeposited GMR materials where advantages of electrodeposition over vacuum deposition methods have been discussed. Ross describes the two approaches that have been used to fabricate nanosize multilayer GMR films by electrodeposition - the single bath and the dual bath methods.

Although there have been many investigations on the electrodeposition of GMR multilayers, most were limited

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to determining dependence of the GMR effect on layer thickness. In order to develop highly sensitive GMR materials, studies are needed to determine the relationships between electrodeposition conditions and the electrical and magnetic properties of deposits. In this work, Co/Cu multilayers were electrodeposited by the dual bath method. The dependence of electrical resistivity (ρ) on electrodeposition conditions and Co/Cu thickness have been investigated. The effect of these condition on GMR ($\Delta\rho/\rho$), sensitivity ($d(\Delta\rho/\rho)/dH$), coercivity (H_c), remanence (M_R), magnetic saturation (M_S) and saturation field (H_S) are also reported.

2. Experiments

It is generally known that the solution composition and deposition conditions have considerable effects on deposit properties. An important consideration in the electrodeposition of Co/Cu multilayers is the selection of plating solutions which prevent cobalt dissolution and create sharp interfaces between the cobalt and copper layers. Acid copper sulfate (bath A) and alkaline copper pyrophosphate (bath B) baths were selected as copper plating solutions. Acid cobalt sulfate (bath C) and alkaline cobalt pyrophosphate (bath D) baths were used to electrodeposit cobalt layers. Plating solution compositions and deposition conditions investigated are given in Table 1. Solution pH was adjusted with either H_2SO_4, H_3PO_4, NaOH, or NH_4OH. The solutions were unstirred at room temperature. A current density (CD) of 5 mA cm^{-2} was applied. Current efficiencies were determined by dissolving the deposits in 30% nitric acid and analyzing the deposit content using atomic absorption spectrophotometry. Current efficiencies enable layer thicknessess to be precisely controlled by adjusting the deposition charge. Most of the deposited multilayers consisted of at least 200 Co/Cu paired layers; when the number of layers was large, GMR and sensitivities were found not to depend on the exact number of layers.

Magnetic properties, including giant magnetoresistance (GMR) and hysteresis loops, were measured in both parallel (//) and perpendicular ($\perp$) directions between film surface and magnetic field by a vibrating sample magnetometer (Model 1660, ADE Tech.).

3. Results and Discussion

Two copper plating solutions were initially investigated to determine the possible displacement reaction (i.e. $Co+Cu^{2+}=Co^{2+}+Cu$) which can be a problem in the fabrication of sharply defined multilayers with controlled individual layer thickness. The acid copper sulfate solution (bath A) with additives produced bright nano-thick contiguous layers; however, significant amounts of cobalt dissolved during copper deposition. Slightly alkaline copper pyrophosphate solutions (bath B) also produced nano-thick bright contiguous layers with no attack or immersion deposition on the cobalt deposits. Co/Cu multilayers were electrodeposited from the two copper plating solutions to compare their effects on GMR and other magnetic properties; cobalt layers were electrodeposited from acid cobalt sulfate baths (bath C). The partial dissolution of the cobalt layers during copper deposition from acid copper sulfate baths was clearly evident. Further, lower GMR and higher coercivities were obtained compared to deposits using the alkaline copper pyrophosphate baths. The lower GMR might be attributed to intermixing between the cobalt and copper layers and roughing of the interfaces due to copper immersion deposition. Based on the above studies, we concluded that copper pyrophosphate baths are superior to acid copper sulfate baths to produce distinct Co/Cu multilayers with higher GMR.

The effects of acid and alkaline cobalt plating solutions on the properties of Co/Cu multilayer deposits were investigated. The current efficiency (CE) of the acid cobalt sulfate solution (bath C) was 69% compared to 55% for the cobalt pyrophosphate solution (bath D). However, nano-thick contiguous cobalt films deposited more rapidly from the cobalt pyrophosphate bath (bath D) than from the cobalt sulfate bath (bath C).

Figs. 1 and 2 show the dependence of a) GMR, b) sensitivity, c) coercivity and d) electrical resistivity on copper layer thicknesses when the Co layers were electrodeposited from cobalt sulfate baths (bath C, Fig. 1) and from cobalt pyrophosphate baths (bath D, Fig. 2). Cobalt layer thicknesses were fixed at 4.5 and 9 nm. Figs. 1 and

Table 1. Plating solution compositions (room temperature).

Bath \ Metal	Solution Composition	pH	CD ($mAcm^{-2}$)	CE (%)
A. Cu(Acid)	0.8 M $CuSO_4$ + 0.5 M H_2SO_4 + 100 ppm NaCl + 1 v/v % commercial brightner	<1	5	100
B. Cu(Alkaline)	0.12 M $CuSO_4$ + 0.45 M $Na_4P_2O_7$ + 1 ml/L NH_4OH	8.5-9	3-10	48
C. Co(Acid)	0.2 M $CoSO_4$ + 0.5 M H_3BO_3	3-4	5	69
D. Co(Alkaline)	0.12 M $CoSO_4$ + 0.45 M $Na_4P_2O_7$ + 1 ml/L NH_4OH	8.5-9	3-10	55

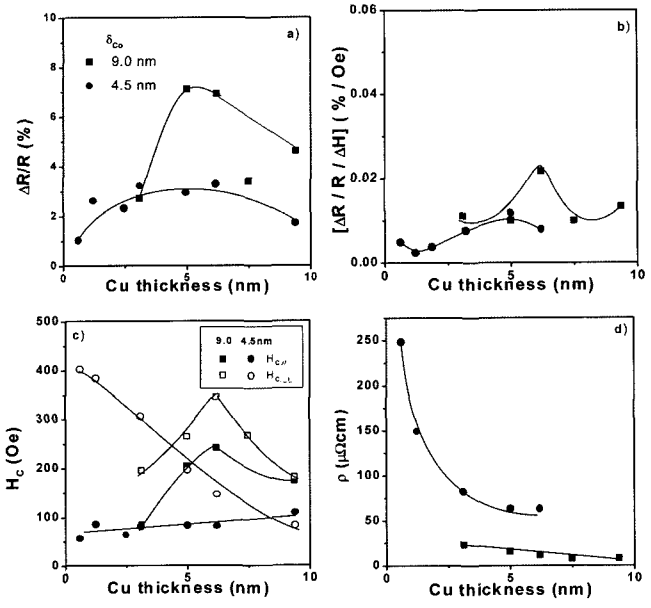

Fig. 1. The dependence of a) GMR, b) sensitivity, c) coercivity and d) electrical resistivity on Cu layer thickness: Cu layers (bath B) and Co layers (bath C), δ_{Co}=9.0 and 4.5 nm.

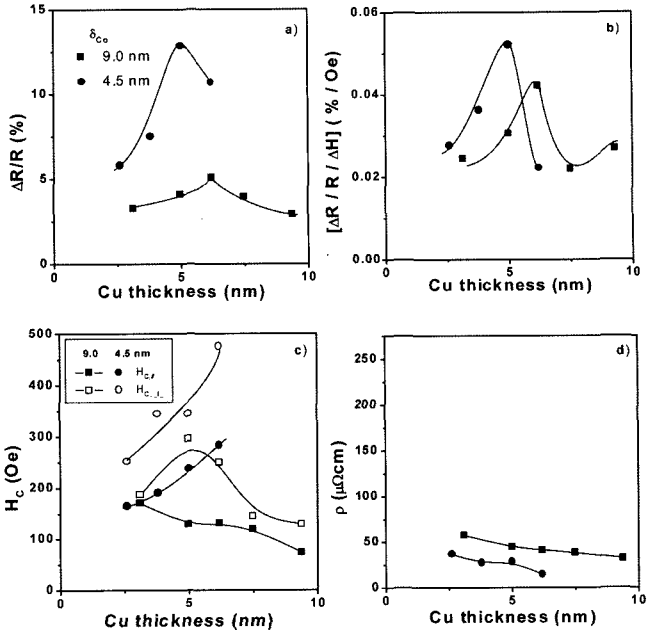

Fig. 2. The dependence of a) GMR, b) sensitivity, c) coercivity and d) electrical resistivity on Cu layer thickness: Cu layers (bath B) and Co layers (bath D), δ_{Co}=9.0 and 4.5 nm.

2 indicate that acid sulfate and alkaline pyrophosphate solutions resulted in deposits with significantly different properties. Giant magnetoresistance (GMR) and sensitivities increased with increased cobalt layer thicknesses deposited from sulfate baths (Fig. 1a & b). A maximum GMR of 2.5% and sensitivity of 0.01%/Oe were obtained with 5 nm thick Cu/4.5 nm thick Co layers. When the Co layer thickness was increased to 9 nm, maximum GMR (7%) and sensitivity (0.02%/Oe) were obtained. In contrast to deposits from acid sulfate baths, both GMR and sensitivity increased with decreasing cobalt layer thicknesses deposited from cobalt pyrophosphate baths (Fig. 2a & b). A maximum GMR of 12% and sensitivity of 0.052%/Oe were obtained at 5 nm thick Cu/4.5 nm thick Co layers. As the cobalt layer thickness was increased to 9 nm, a lower maximum GMR of 5% and sensitivity of 0.042%/Oe were obtained at 6.2 nm thick copper layers. In addition to significant differences in GMR and sensitivity of the multilayers from the different cobalt plating solutions, other magnetic properties and electrical resistivity were also influenced. Figs. 1c and 2c compare the effects of solution compositions, and copper and cobalt layer thicknesses on the coercivities ($H_{C,//}$ and $H_{C,\perp}$) of the deposits. The electrical resistivity decreased substantially for 4.5 nm Co layers compared to only a slight decrease for 9 nm Co layers from sulfate baths (Fig. 1d). From pyrophosphate baths, electrical resistivity of Co/Cu multilayers with 4.5 nm Co layers were lower than multilayers with 9 nm Co layers where electrical resistivity decreased with increasing copper thicknesses.

These opposing trends might be attributed to the electrodeposition of contiguous nano- thick films. Based on visual observations, Co from pyrophosphate baths formed nano-thick contiguous films more rapidly than from sulfate baths. The ability of plating solutions to form contiguous layers at low nano thicknesses is crucial to achieving highly sensitive GMR multilayers. In addition, deposits from acid sulfate baths have larger grains than from alkaline pyrophosphate baths. This is presumably because, generally, deposits from complexing solutions exhibited finer grains. Further, the acidity of cobalt sulfate baths may cause etching resulting in rougher copper layers and poor GMR effects with higher electrical resistivity.

Figs. 3 and 4 show the dependence of GMR, sensitivity and saturation field (H_S), coercivity, and electrical resistivity on Co layer thickness where Co layers were electrodeposited from sulfate baths (bath C, Fig. 3) and from pyrophosphate baths (bath D, Fig. 4). Cu layer thicknesses were fixed at 6.2 nm. Maximum GMR (10% from sulfate bath and 11% from pyrophosphate bath) was obtained at approximately 5 nm, then decreasing with increasing Co thickness (Figs. 3a and 4a). Maximum coercivity was obtained at 13 nm thickness in the parallel ($H_{C,//}$) and 18 nm thickness in the perpendicular ($H_{C,\perp}$) direction from sulfate bath deposits (Fig. 3c). However, both parallel and perpendicular coercivities decreased with increasing Co deposit thickness from pyrophosphate

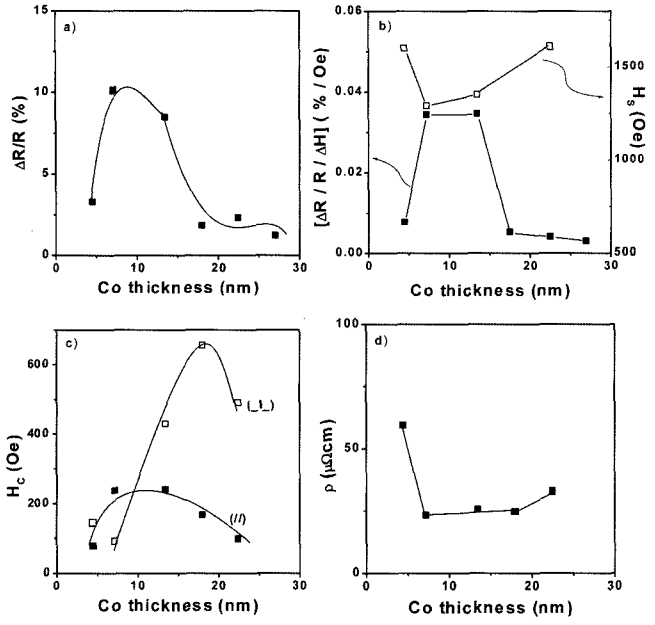

Fig. 3. The dependence of a) GMR, b) sensitivity, c) coercivity and d) electrical resistivity on Co layer thickness: Cu layers (bath B) and Co layers (bath C), δ_{Cu}=6.2 nm.

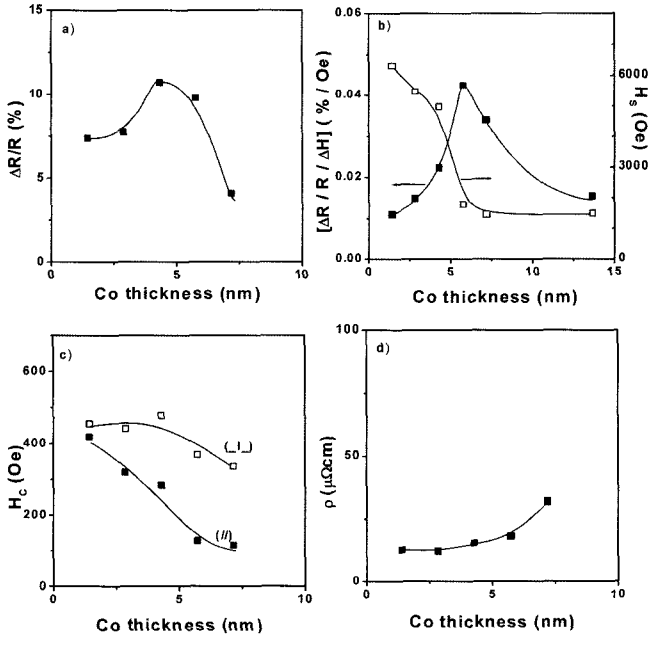

Fig. 4. The dependence of a) GMR, b) sensitivity, c) coercivity and d) electrical resistivity on Co layer thickness: Cu layers (bath B) and Co layers (bath D), δ_{Cu}=6.2 nm.

baths (Fig. 4c). Electrical resistivities of deposits from sulfate baths were greater than from pyrophosphate baths; electrical resistivities increased with increasing Co thickness in both cases. Figs. 3b and 4b show the dependence of sensitivities and saturation fields on Co layer thicknesses. Deposits from both sulfate and pyrophosphate

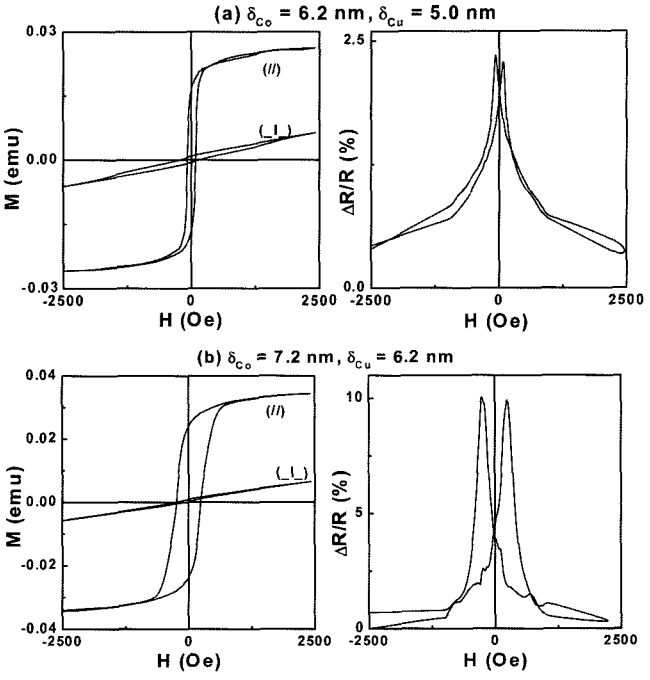

Fig. 5. Hysteresis loops and GMR curves a) δ_{Co}=6.2 and δ_{Cu}=5.0 nm, b) δ_{Co}=7.2 and δ_{Cu}=6.2 nm: Cu layers (bath B) and Co layers (bath C).

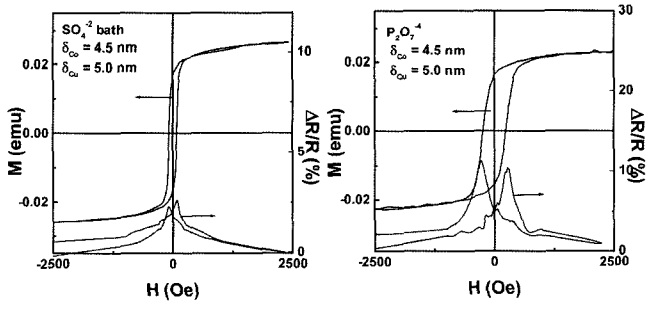

Fig. 6. Hysteresis loops and GMR curves of Co/Cu multilayers in parallel direction (//) from Co sulfate and Co pyrophosphate baths.

baths exhibited maximum sensitivities at 5-6 nm thick Co layers.

Fig. 5 shows hysteresis loops and GMR curves from Co sulfate baths, which indicated that the easy axis was parallel to the substrate. Squareness (M_R/M_S) was higher than reported data from vacuum processes. Rupp and Schuster reported that GMR effects were linearly related to 1-M_R/M_S, where 1-M_R/M_S represents the fraction of the Co which is antiferromagnetically coupled [8].

Fig. 6 shows the comparisons of hysteresis loops and GMR curves of deposits from Co sulfate and pyrophosphate baths at nearly identical layer thicknesses: Cu=5 nm and Co=4.5 nm. Hysteresis loops were relatively square; coercivity of deposits from pyrophosphate bath

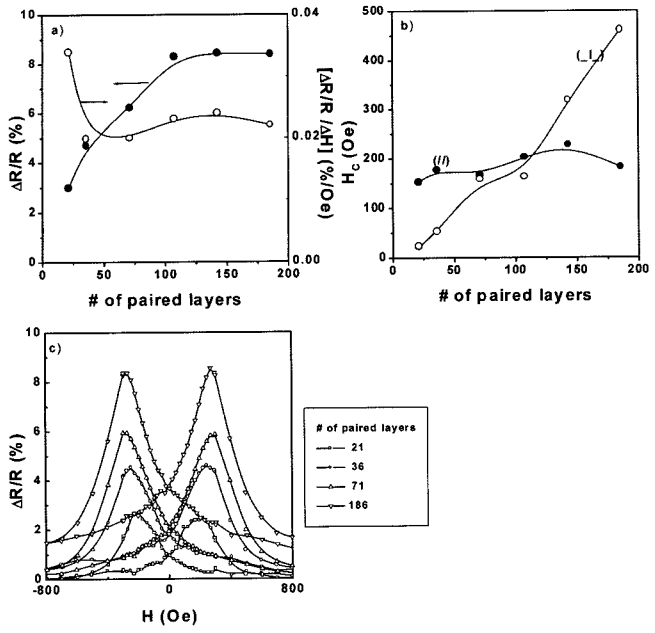

Fig. 7. The dependence of a) GMR and sensitivity, and b) coercivity, and c) GMR curves on number of Co/Cu paired layers: Cu layers (bath B) and Co layers (bath D), δ_{Cu}=5 nm and δ_{Co}=4.5 nm.

was greater than from sulfate baths.

The number of Co/Cu paired layers were also varied to determine their effect on GMR, sensitivity and coercivity, with individual Co and Cu layer thickness fixed at 4.5 and 5 nm, respectively. GMR increased with increase in the number of paired layers while sensitivities decreased. However, beyond 200 layers, GMR and sensitivities were independent of further increases (Fig. 7a). Parallel coercivities were independent of the number of layers while perpendicular coercivities increased almost linearly with increasing numbers of layers (Fig. 7b). Fig. 7c shows the dependence of GMR on the number of layers.

4. Conclusion

The effect of electrodeposition conditions with various plating solutions on the magnetic properties of Co/Cu multilayers was studied. Magnetic and electrical properties were greatly influenced by solution compositions. Alkaline copper pyrophosphate baths produce nano-thick bright contiguous layers without immersion copper coating. Contiguous cobalt layers were formed more rapidly from alkaline cobalt pyrophosphate baths than from cobalt sulfate baths.

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